First-principles calculations of shocked fluid helium in partially ionized region

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Abstract

Quantum molecular dynamic simulations have been employed to study the equation of state (EOS) of fluid helium under shock compressions. The principal Hugoniot is determined from EOS, where corrections from atomic ionization are added onto the calculated data. Our simulation results indicate that principal Hugoniot shows good agreement with gas gun and laser driven experiments, and maximum compression ratio of 5.16 is reached at 106 GPa.

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I. INTRODUCTION

High-pressure introduced response of materials, which requires accurate understandings of the thermophysical properties into new and complex region, has gained much scientific interest recently [1]. The relative high temperature and high density are usually referred as the so-called "warm dense matter" (WDM)- a strongly correlated state, where simultaneous dissociations, ionizations, and degenerations make modelling of the dynamical, electrical, and optical properties of WDM extremely challenging [2]. WMD, which provides an active research platform by combining the traditional plasma physics and condensed matter physics, usually appears in shock or laser heated targets [3], inertial confinement fusion [4], and giant planetary interiors [5].

Next to hydrogen, helium is the most abundant element in the universe, and physical properties of warm dense helium, especially the EOS, are critical for astrophysics [6, 7]. For instance, the structure and evolution of stars, White Dwarfs, and Giant Planets [8–11], and therefore the understanding of their formation, depends sensitively on the EOS of hydrogen and helium at several megabar regime. For all planetary models, accurate EOS data are essential in solving the hydrostatic equation. As a consequence, a series of experimental measurements and theoretical approaches have been applied to investigate the EOS of helium. Liquid helium was firstly single shocked to 15.6 GPa using two stage light gas gun by Nellis et $al.$, then double shocked to 56 GPa, and the calculated temperature are 12000 and 22000 K respectively [12]. Maximum compression ratio ($\eta_{max} \approx 6$) was achieved by laser driven shock experiments with the crossover pressure around 100 GPa [13], However, soon after that, Knudson et $al.$ have modified η_{max} to be 5.1 [14]. Theoretically, since the ionization equilibrium is not interfered with the dissociation equilibrium between molecules and atoms, helium, which is characterized by monoatomic molecule and close shell electronic structure, is particularly suitable for the investigation of the high pressure behavior under extreme conditions. Free energy based chemical models by Ross et $al.$ [15], Chen et $al.$ [16], and Kowalski et $al.$ [17] have been used to investigate the principal Hugoniot of liquid helium, and the results are accordant with gas gun experiments. However, considerable controversies have been raised at megabar pressure regime, especially since the data was probed by laser shock wave experiments. Interatomic potential method predict $\eta_{max}=4$ for shock compressed helium [15], whereas, the EOS used by the astrophysical community

from Saumon *et al.* (SCVH) [8], path-integral Monte Carlo (PIMC) [18], and activity expansion (ACTEX) [19] calculations provide an increase in compressibility at the beginning of ionization. For the initial density of ρ_0=0.1233 g/cm^3, SCVH and ACTEX simulation results indicate the maximum compression ratio lies around 6 at 300 GPa and 100 GPa respectively [8, 19], while PIMC calculations suggest η_{max}=5.3 near 360 GPa [18].

On the other hand, quantum molecular dynamic (QMD) simulations, where quantum effects are considered by the combinations of classical molecular dynamics for the ions and density functional theory (DFT) for electrons, have already been proved to be successful in describing thermophysical properties of materials at complex conditions [20, 21]. However, the DFT based molecular dynamic simulations (with or without accounting for excited electrons) do not provide reasonable results at the ionization region, mainly because the atomic ionization is not well defined in the framework of DFT. Considering these facts mentioned above, thus, in the present work, we applied the corrected QMD simulations to study shock compressed helium, and the EOS, which is compared with experimental measurements and different theoretical models, are determined for a wide range of densities and temperatures. The calculated compression ratio is substantially increased according to the ionization of atoms in the warm dense fluid.

II. COMPUTATIONAL METHOD

The Vienna Ab-initio Simulation Package (VASP) [22, 23], which was developed at the Technical University of Vienna, has been employed to perform simulations for helium. The elements of our calculations consist of a series of volume-fixed supercells including N atoms, which are repeated periodically throughout the space. By involving Born-Oppenheimer approximation, electrons are quantum mechanically treated through plane-wave, finite-temperature (FT) DFT [24], where the electronic states are populated according to Fermi-Dirac distributions at temperature T_e. The exchange-correlation functional is determined by generalized gradient approximation (GGA) with the parametrization of Perdew-Wang 91 [25]. The ion-electron interactions are represented by a projector augmented wave (PAW) pseudopotential [26]. Isokinetic ensemble (NVT) is adopted in present simulations, where the ionic temperature T_i is controlled by Nośe thermostat [27], and the system is kept in local equilibrium by setting the electron (T_e) and ion (T_i) temperatures to be equal.

The plane-wave cutoff energy is selected to be 700.0 eV so that the pressure is converged within 3% accuracy. Γ point is used to sample the Brillouin zone in molecular dynamics simulations, because EOS can only be modified within 5% for the selection of higher number of **k** points. 64 helium atoms are included in the cubic supercell. The densities selected in our simulations range from 0.1233 to 0.8 g/cm^3 and temperatures between 4 and 50000 K, which highlight the regime of the principal Hugoniot. All the dynamic simulations are lasted for 6000 steps, and the time steps for the integrations of atomic motion are selected according to different densies (temperatures) [28]. Then, the subsequent 1000 steps of smulation are used to calculate EOS as running averages.

III. RESULTS AND DISCUSSION

Different corrections to QMD simulations have already been used to model the thermophysical properties of WDM, such as the zero point vibrational energy modification for hydrogen and deuterium [29]. However, quantitative descriptions of the ionization of atoms in the frame of DFT is still lacking, except for the Drude model for aluminium introduced by Mazevet *et al.* [30], but the simple metallic model is not suitable for studying warm dense helium. Here, we adopt similar approximations as described in Ref. [31], where the effect of atomic ionization are considered, to study the EOS of fluid helium. In standard FT-DFT molecular dynamic simulations, the ionization energy is excluded, thus the EOS should be corrected as [31]:

$$E = E_{QMD} + N\beta E_{ion}, \tag{1}$$

$$P = P_{QMD} + (1 + \beta)\frac{\rho k_B T}{m_{He}}, \tag{2}$$

where E_{QMD} and P_{QMD} are data obtained from regular QMD calculations, and N is the total number of atoms considered in supercells. m_{He} and k_B represent the mass of helium atom and Boltzmann constant. The density and temperature are denoted by ρ and T, respectively. β stands for the ionization degree, and E_{ion} is the ionization energy.

In the present work, only the first ionization level is considered, and the ionization degree of helium can be evaluated through Saha equation:

$$\frac{\beta^2}{1 - \beta} = \frac{2\Omega}{\lambda^3} \exp\left(-\frac{E_{ion}}{k_B T}\right), \tag{3}$$
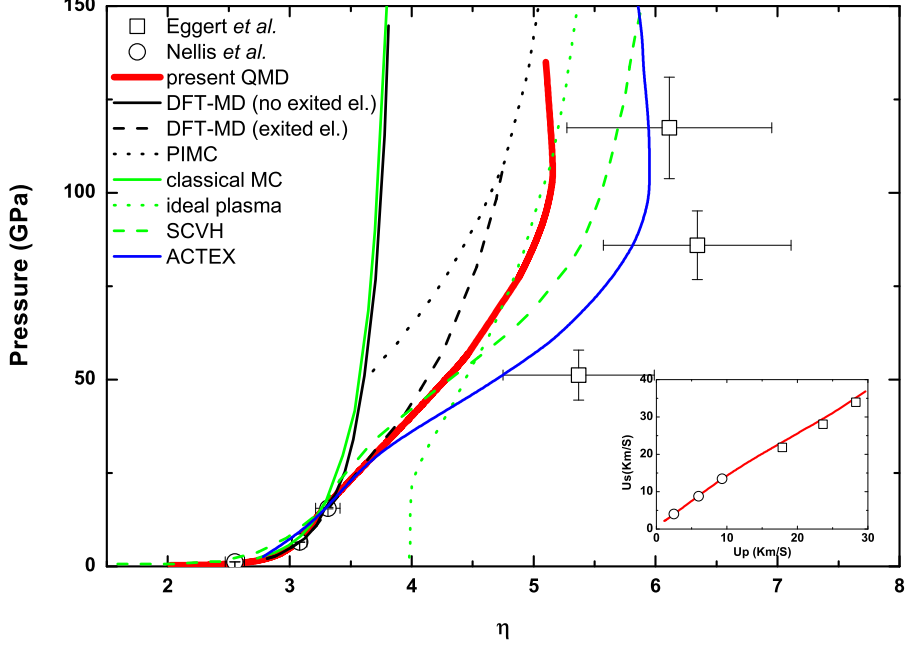
FIG. 1: (Color online) Principal Hugoniot up to 130 GPa is shown for the present work (red line), where previous theoretical predictions and experimental measurements are also shown for comparison. Experiments: Two stage light gas gun data [12] is denoted by open circle; Laser driven experimental results [13] are labelled by open square. Theories: (i) Classical MC simulation results [32] are plotted as green solid line; (ii) ideal plasma's Hugoniot curve [18] is shown as green dotted line; (iii) SCVH method [8] is labelled as green dashed line; (iv) ACTEX results [19] are blue solid line; (v) Previous DFT simulation results [18] (with and without accounting for electron excitation) are shown as black dashed and solid line, respectively; (vi) PIMC results [18] are labelled as black dotted line. Inset is the plot of shock wave velocity verse mass velocity.

$$\lambda = \sqrt{\frac{h^2}{2\pi m_e k_B T}}, \tag{4}$$

where, m_e and Ω present the mass of electron and volume of the supercell. The ionization energy E_{ion} is determined by $E_{ion} = E^{He+}(\rho, T) - E^{He}(\rho, T)$, where $E^{He+}(\rho, T)$ and $E^{He}(\rho, T)$ are total energy of He$^+$ and He at the relative density and temperature, respectively.

Based on the approximations mentioned above, the calculated EOS was examined theoretically along the principal Hugoniot, the locus of states that satisfy the Rankine-Hugoniot (RH) equations, which are derived from conservation of mass, momentum, and energy across the front of shock waves. The RH equations describe the locus of states in (E, P, V)-space
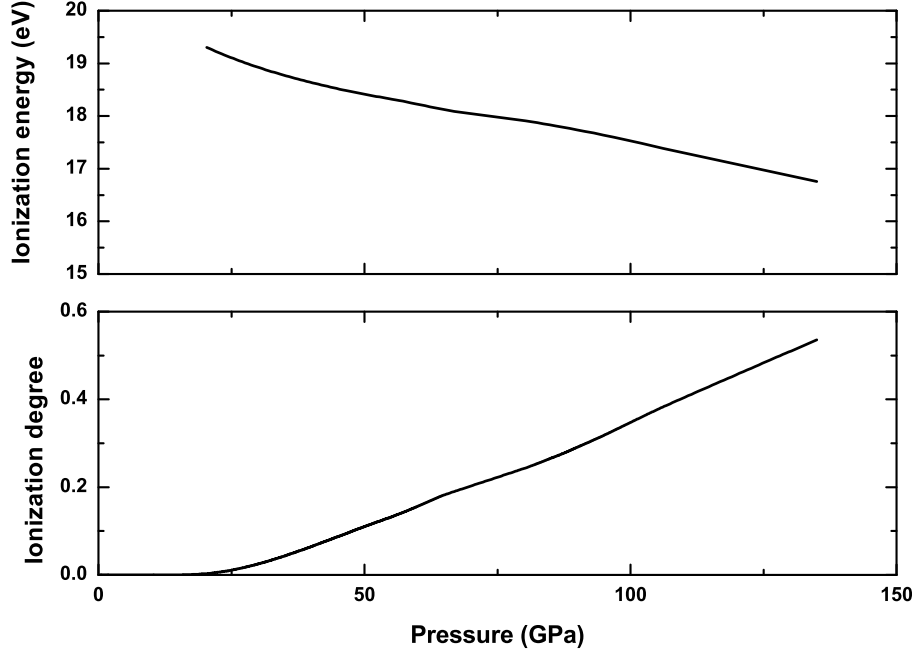
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FIG. 2: Ionization energy and ionization degree are plotted as functions of pressure along the principal Hugoniot in the upper and lower panels, respectively.

satisfying the following relation:

$$E_1 - E_0 = \frac{1}{2}(P_1 + P_0)(V - V_0),　(5)$$

$$P_1 - P_0 = \rho_0 u_s u_p,　(6)$$

$$V_1 = V_0(1 - u_p/u_s),　(7)$$

where E, P, V present internal energy, pressure, volume, and subscripts 0 and 1 present the initial and shocked state, respectively. In Eqs. (6) and (7), u_s is the velocity of the shock wave and u_p corresponds to the mass velocity of the material behind the shock front. In our present simulations, the initial density for helium is ρ_0=0.1233 g/cm^3 and the liquid specimen is controlled at a temperature of 4 K, where the internal energy is E_0=-0.02 eV/atom. The initial pressure P_0 can be treated approximately as zero compared to the high pressure of shocked states along the Hugoniot. The Hugoniot points are obtained as follows: (i) smooth functions are used to fit the internal energy and pressure in terms of temperature at sampled density; (ii) then, Hugoniot points are derived from Eq. (5).

The principal Hugoniot curve for helium is shown in Fig. 1, where previous experimental measurements and theoretical predictions are also plotted for comparison. For pressures be-
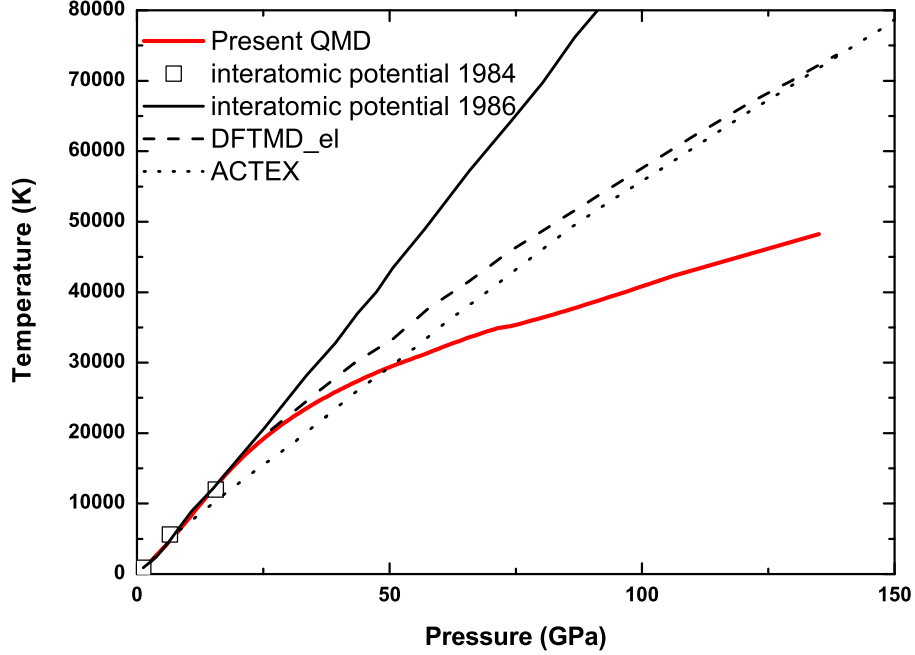
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FIG. 3: (Color online) Comparison between our calculated shock temperature and previous theoretical predictions. Interatomic potential results are shown as open square [12] and solid line [15]; DFT [18] and ACTEX [19] results are plotted as dashed and dotted line, respectively.

low 30 GPa, our results show good agreements with the data detected by gas gun experiments [12]. At higher pressures, the principal Hugoniot curve shows a maximum compression ratio $\eta_{max} \approx 6$ with the crossover pressure around 100 GPa, as have been reported by laser driven experiments [13]. Soon after that, the use of quartz as a shock wave standard by Knudson *et al.* has improve the shock data, and η_{max} has been reduced to be 5.1 [14]. Our corrected QMD simulation results indicate that, the atomic ionization dominates the characteristic of the EOS at $P > 30$, and the principal Hugoniot shows soften behavior with the increase of pressure, then reach its maximum ($\eta_{max} = 5.16$) with the corresponding pressure of 106 GPa. Then, stiff behavior has been found at $P > 110$ GPa along the Hugoniot. As has been shown in Fig. 2, with the increase of pressure along the Hugoniot, ionization energy decreases, and continuous increase of atomic ionization has become considerable in determining the EOS of fluid helium. Maximum compression ratio is achieved with the ionization degree of 40%. The wide-range behavior of our simulated principal Hugoniot for helium shows excellent agreement with experimental ones.

Concerning other theoretical models, classical MC results show stiff behavior along the

Hugoniot, and η_{max} lies around 4 at 1000 GPa [32]. Direct DFT simulation results show stiff behavior up to 110 GPa, while, by combining PIMC simulations, η_{max} was reported to be 5.3 at 360 GPa [18], but the predicted pressure is still too high compared with laser driven experiments. ACTEX [19] and SCVH [8] calculations predict η_{max} to be 6 near 100 GPa and 300 GPa respectively, but the results do not agree with those of Knudson *et al.* [14].

Temperature, which is focused as one of the most important parameters in experiments, is difficult to be measured because of the uncertainty in determining the optical-intensity loss for ultraviolet part of the spectrum in adiabatic or isentropic shock compressions, especially for the temperature exceeding several electron-volt [33]. QMD simulations provide powerful tools to predict shock temperature. The calculated Hugoniot temperature has been shown in Fig. 3 as a function of pressure along the Hugoniot. Previous theoretical predictions, such as interatomic potential [12, 15], DFT-MD (excited electron) [18], and ACTEX [19] are also provided for comparison. Disagreements have been found to begin at around 30 GPa with the relative temperature of 20000 K, which highlights the starting point of ionization on the Hugoniot, and the predicted temperatures by those models are higher at a given pressure compared with our calculations.

IV. CONCLUSION

In summary, We have performed DFT based QMD simulations to study the thermophysical properties of helium under extreme conditions. The Hugoniot EOS has been evaluated through QMD calculations and corrected by taking into account the atomic ionization described by Saha equation, where only first ionization is considered. The corrected Hugoniot has been proved accord well with the experimental data in a wide range of shock conditions, which thus indicates the importance of atomic ionization. Maximum compression ratio of 5.16 reveals at round 106 GPa along the principal Hugoniot, and the softened characteristic of the Hugoniot has been demonstrated by the contributions from atomic ionization.

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